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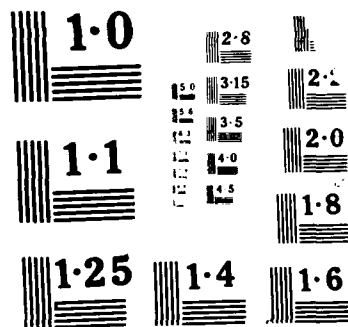
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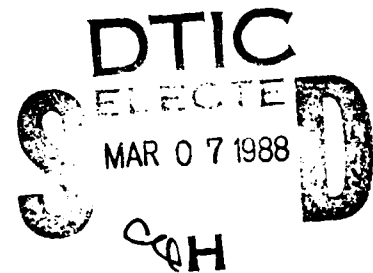
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The Application of SERS to Study
Surface Oxidation Reactions
of Phosphonates

by

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THE APPLICATION OF SERS TO STUDY SURFACE OXIDATION REACTIONS OF PHOSPHONATES

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ABSTRACT

Surface enhanced Raman scattering has developed into an important spectroscopic tool in the identification of adsorbates on Ag, Cu, or Au under in situ conditions. This paper describes the first use of this technique to study the kinetics of surface enhanced catalysed chemical reactions. The reaction of NO_2 gas with Ag powder is shown to proceed through the formation of AgNO_2 which autocatalytically decomposes into AgNO_3 , NO and free Ag which forms Ag microstructures. Recent experiments to elucidate the reactions of DMMP at these catalytically active sites show that H_2PO_4^- and HPO_4^{2-} are formed on the surface at room temperature. The use of dynamically produced active Ag sites as active filters for phosphonates is discussed.

INTRODUCTION

The study of in situ solid-gas interfacial oxidation or reduction phenomena has been hampered by the lack of adequate spectroscopic probes which provide detailed information about the molecular parameters of the adsorbates on the solid surface during the chemical reactions. Well-developed tools such as LEED, EELS, Auger, and other similar spectroscopies measure the properties of the vacuum-solid interface which are of great interest, but which may not be simply related to those of in situ conditions. Even IR spectroscopy is difficult to apply to surface adsorbates because there is no simple method to diminish the strong absorptions of the substrates in the presence of the signals due to the adsorbates.

Raman spectroscopy has not been thought to be useful since the cross section for Raman scattering is inherently low. Assuming 10^{19} molecules/m² and a strong scatterer such as pyridine, the Raman scattering intensity due to the adsorbate is just barely detectable even after integration times of 1000 s.[1] It was not surprising that great interest was shown in a 1977 report that the Raman scattering efficiency of pyridine adsorbed on Ag metal was a million times that calculated from the bulk properties.[2,3] Given the acronym SERS, surface enhanced Raman scattering has rapidly become an effective probe for the identification of adsorbates at gas-metal interfaces.

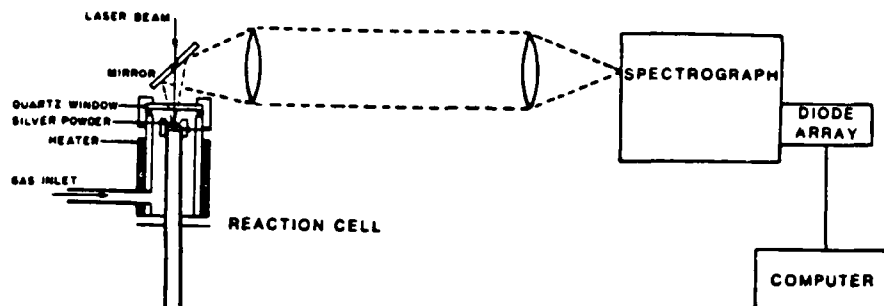


Figure 1

This paper is a report of recent experiments using SERS to not only identify adsorbates, but to measure the rate of surface chemical reactions in in situ real-time conditions. The kinetic studies provide insight into the details of the surface reactions with elementary gases at room and elevated temperatures. It is this information which is of importance in the design of effective filters for gas purification by the obviation of noxious vapors.

The apparatus used to measure SERS is shown in Fig. 1. An argon ion laser source is focused on the sample which is a Ag powder with an average size of about 1 micron. The inelastically scattered Raman light is focused on the entrance slit of a triple-stage spectrograph used to reject the strong laser line at a frequency of f_0 and to disperse the extremely weak Raman light at f_r . At the exit plane of the spectrograph, a linear diode array detector with 700 discrete elements, intensified by a microchannel electronmultiplier, is used₁ to simultaneously detect the Raman light within a spectral region of 1500 cm^{-1} . Typically, the time required for measurement is approximately 0.5 s for a Raman signal with S/N of 50. However, the time interval between the initiation of two scans is about 1.5 s because of the long time interval used in the storage of the data on the floppy disk. Presumably with the development of new control circuitry with and using 1M RAM storage, the shortest time interval between spectral frames will be <0.5 s.

Strong SERS signals have been observed from adsorbates on several substrates made from the coinage metals, Au, Ag, Cu, the alkali metals, and the pseudo silver metal-hydride, Pd(H). Each of these systems provides important information about the mechanisms for the enhancement of the Raman signal of the adsorbate. A necessary condition is the presence of surface roughness on the submicroscopic and atomic scale. Two mechanisms are currently thought to contribute to the enhancement factor of 10^4 to 10^6 in the SERS effect. [4]

The first mechanism uses the classical theory of the interaction of electromagnetic waves with microstructures of metals which have complex dielectric constants. All of the molecules adsorbed on the surface of a metal particle will experience an augmented electric field because the real part of the dielectric constant, which is negative, cancels a term in the dielectric constant due to the fluid in which the particle is embedded. Since this cancellation occurs in the denominator, the field at the surface is about 1000 times that of the incident field for the case of Ag. The same enhancement occurs for the field of the scattered light. The effect of these fields appears as an augmented polarizability which in turn manifests itself as a strong Raman signal. The range of Ag particle sizes which effectively enhances the field of a visible laser radiation at the surface is centered at



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20 nm.

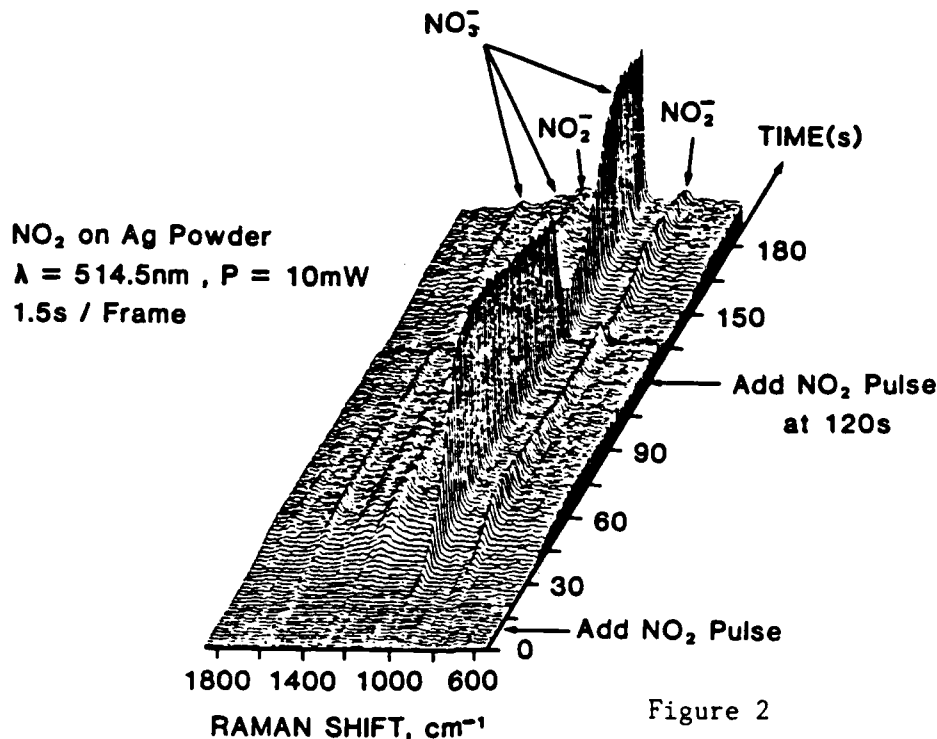
The second mechanism uses a quantum mechanical model in which the adsorbate forms a 'molecule' with surface adatoms or clusters of a few atoms with spatial dimensions of 1 nm. Upon excitation by the laser, electrons near the Fermi surface are excited to states above the Fermi surface, leaving a hole state behind. The electron may tunnel into the molecule to form the molecule negative ion. The meta stable ion exists for a few vibrations before the electron tunnels back before it recombines with the hole state. If the molecule is left in an excited vibrational state, the luminescence of the electron-hole recombination will occur at a frequency shifted from the laser frequency, f_0 , by an amount equal to the molecular vibrational frequency, f_v . Atomic scale roughness provides both active sites for the adsorption of the molecules and a mechanism for non-vertical transitions due to the loss of k-space momentum.

Since adatoms occur on the 20 nm microstructures, it is reasonable to assume that both enhancement mechanisms are operative: that the electric field is enhanced, and the adatom-molecular process occurs through electric-dipole processes. The overall enhancement factor is the product of the two separate enhancement factors which may vary during a surface chemical reaction. Exothermic chemical reactions cause the surface to reform. Adatoms will move to kinks, edges, and vacancies to be lost as sites for the enhancement process. Depending on the surface chemical processes, new adatoms may be formed with new adsorbates in the vicinity and producing new SERS signals. If the heating is mild, the larger 20 nm structures will persist. If the thermal energy of the chemical reaction is contained in a surface layer causing extensive melting then the SERS signal intensity will decrease drastically.

THE REACTION OF $\text{NO}_2/\text{N}_2\text{O}_4$ WITH Ag METAL

An example of a surface chemical reaction which illustrates these ideas is the heterogeneous catalytic reaction of $\text{NO}_2/\text{N}_2\text{O}_4$ with Ag metal powders. The overall thermodynamic exothermic reaction is: $4\text{Ag} + \text{NO}_2 = \text{AgNO}_3 + \text{NO}$. It has been shown [5,6] using SERS that the initial reaction of NO_2 with Ag proceeds exothermally with the formation of the nitrite, AgNO_2 . $\text{Ag} + \text{NO}_2 = \text{AgNO}_2$. Any oxide or carbonate on the surface is displaced or forms AgNO_3 . AgNO_2 undergoes an autocatalytic endothermic reaction on Ag according to: $2\text{AgNO}_2 = \text{AgNO}_3 + \text{NO} + \text{Ag}$. The Ag produced in this reaction migrates in the matrix of AgNO_3 at room temperature to form Ag microstructures which provide sites for the SERS enhancement mechanisms and further catalytic activity. This reaction sequence is shown in Fig. 2 where the SERS spectra as a function of time is shown after a pulse of NO_2 has been added to a Ag powder surface.

Initially there is no SERS spectra because of the absence of surface roughness which provides proper sites for the enhancement mechanism to be operative. Upon the addition of the pulse of NO_2 gas, a strong signal at 1045 cm^{-1} slowly appears which is due to the formation of AgNO_3 near a SERS active Ag site. The SERS active sites are generated by the autocatalytic decomposition of AgNO_2 as described previously. Other signals also appear due to the formation of AgNO_2 in the vicinity of the active SERS site. The NO_2^- peaks at 819 cm^{-1} as well as at 1285 cm^{-1} serve as measures of the concentration of the NO_2^- adsorbates convoluted by the concentration of Ag SERS active sites and the details of the mechanism of enhancement.

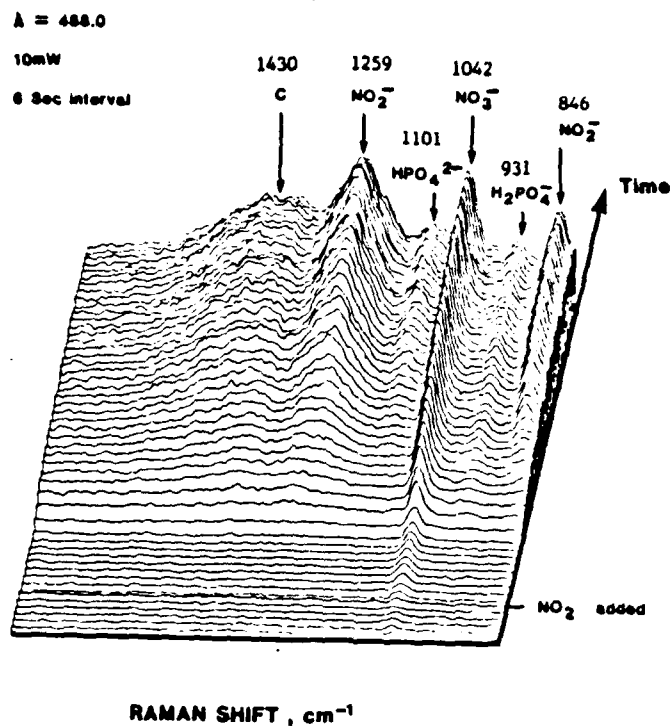


The addition of a second pulse of NO₂ gas to this prepared system has interesting consequences as shown in Fig. 2. The SERS signal due to NO₃⁻ at 1045 cm⁻¹ decreases in intensity. It is as though NO₂ has chemically reduced the NO₃⁻ ions, contrary to the chemistry of these species. Actually, the second pulse of NO₂ reacts with the Ag microstructures forming new AgNO₂ and simultaneously removing the SERS active sites for enhancement mechanisms. Close examination of Fig. 2 shows that the SERS signal due to adsorbed NO₂⁻ momentarily increases in intensity during the initial stage of the gas pulse before it decreases in intensity. This is readily explained by the oxidation of the Ag microstructures by NO₂ forming new adsorbed NO₂⁻, but simultaneously depleting the active sites. The autocatalytic process after the pulse has passed through the reactor regenerates the same spectrum observed previously.

Further confirmation of this model is provided by ellipsometric measurements of the film growth on a polished Ag metal surface after being exposed to NO₂/N₂O₄. A complex index of refraction is obtained which is in conformity with Ag microstructures imbedded in a film of AgNO₃. Electromicroscopy has also been used to show that Ag metal particles are formed. [6]

THE REACTION OF DIMETHYMETHYL PHOSPHONATE WITH Ag MICROSTRUCTURES

The reactions of pure gaseous organophosphorus compounds on Au, Cu or Ag surfaces have not been studied extensively and consequently, little is known about the surface catalyzed decomposition processes. If the reaction composition is complicated, for example, by the addition of O₂ or NO₂ to the gas stream, more varied reactions are to be expected. However, it is expected that the primary products containing phosphorus will be derivatives of phosphoric acid. On Ag surfaces, the carbon products will be graphitic carbon which always occurs giving rise to SERS peaks near 1400 cm⁻¹ and CH_x moieties which will have characteristic SERS peaks near 3000 cm⁻¹.



Dimethyl methyl phosphonate, DMMP, has been used as the primary test chemical because of its innocuous behavior. SERS experiments with freshly prepared Ag powders using AgClO_4 as the starting Ag source and hydrazine as the reductant show weak signals similar to those of neat DMMP due to physisorbed DMMP after being exposed to DMMP vapor for several minutes. The SERS spectrum, which initially has peaks due to adsorbed ClO_4^- on the Ag surface, changes slowly as the DMMP in an unreacted state replaces the weakly adsorbed perchlorate.

More striking experimental results are obtained if Ag powder is exposed to pulses of $\text{NO}_2/\text{N}_2\text{O}_4$ in a N_2 carrier gas after exposure to a pulse of O_2 saturated with DMMP vapor. Figure 3 shows that DMMP reacts with freshly prepared Ag microstructures at room temperature to form products which have strong SERS signals as a function of time in the range of $800\text{--}1800\text{ cm}^{-1}$. Outside of this spectral range at 2919 cm^{-1} a peak due to CH species also grows in intensity. The peaks at 846 cm^{-1} , 1269 cm^{-1} and 1042 cm^{-1} are readily identified as being due to adsorbed NO_2^- and NO_3^- . Two additional sharp peaks at 931 and 1102 cm^{-1} are also readily evident. An additional broad band with a hint of a doublet structure appears centered at 1468 cm^{-1} .

The identification of the peaks may be made by reference to the SERS spectra observed from a Ag cathode immersed in 1M phosphate aqueous solutions at pH values ranging from 1-14. [7] The surface of the Ag is first roughened and reformed by an oxidation-reduction cycle. Adsorbed PO_4^{3-} on Ag is sequentially protonated to give HPO_4^{2-} , H_2PO_4^- and H_3PO_4 as the voltage of the Ag electrode is swept to more negative relative to a saturated calomel electrode. The SERS spectra for each ion adsorbate is characteristic in intensity but less so in frequency. All the adsorbates have nearly the same vibrational frequencies at approximately 1070 , 920 , and 550 cm^{-1} but the intensities are radically different. H_2PO_4^- on a Ag electrode has a strong peak at 920 cm^{-1} whereas HPO_4^{2-} has intense peaks at 1070 and 550 cm^{-1} .

Therefore, the DMMP decomposition product which is evidenced the 931 cm^{-1} peak in Fig. 3 is identified as adsorbed H_2PO_4^- and the 1101 cm^{-1} peak is due to the formation of HPO_4^- adsorbed on the surface. The peak at 2919 cm^{-1} shows similar growth due to adsorbed CH_x species as DMMP breaks up on the Ag microstructures.

Closer examination of the time variation of the relative amplitudes of the peaks due to NO_2^- and NO_3^- in Fig. 3 shows that the concentration of NO_2^- adsorbed on the surface relative to NO_3^- is greater in the presence of DMMP² products than in the absence. Apparently DMMP products stabilize or increase the formation of NO_2^- , a process which will occur if the NO_3^- is involved in the oxidation of the DMMP as an oxygen atom transfer agent.³ Isotopic experiments are needed to elucidate this speculation.

CONCLUSIONS AND FUTURE RESEARCH

It has been shown that Ag microstructure are very reactive sites for the oxidation of phosphonates. Size effects are important. Small Ag microstructures prepared by the autocatalytic decomposition of AgNO_2 are effective catalytic sites as well as SERS active sites. Other Ag systems are being investigated as possible methods for producing active Ag microstructures. Partially reduced Ag_2O is particularly effective as a SERS substrate. This unstable compound at 100°C presumably forms Ag microstructures of the proper size, shape and surface characteristics to be considered as an effective filter material which is an effective filter.

ACKNOWLEDGEMENT

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